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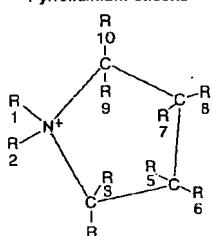
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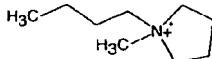
Pyrrolidinium cations



pyrrolidinium ring structure:
R₁-R₁₀ is e.g. H, F, alkylgroup, etc.

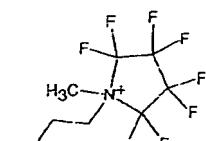
(57) Abstract: An electrochemical element for use at a high temperature has an anode, a cathode comprising an intercalation material having an upper reversible potential-limit of at most 4 V versus Li/Li⁺ as active material, and an electrolyte arranged between the cathode and anode, which electrolyte comprises an ionic liquid with an anion and a cation comprising a pyrrolidinium ring structure having four Carbon atoms and one Nitrogen atom. Experiments revealed that rechargeable batteries comprising such an intercalation material and N-R₁-N-R₂-pyrrolidinium, wherein R₁ and R₂ are alkyl groups and R₁ may be methyl and R₂ may be butyl or hexyl, are particularly suitable for use at a temperature of up to about 150 degrees Celsius and may be used in oil and/or gas production wells.

B



1-butyl-1-methylpyrrolidinium

C



1-butyl-2,2,3,3,4,4,5,5-octafluoro-1-methylpyrrolidinium

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TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
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ELECTROCHEMICAL ELEMENT FOR USE AT HIGH TEMPERATURES

BACKGROUND OF THE INVENTION

This invention relates to an electrochemical element for use at high temperatures.

Electrochemical elements comprise a cathode and an anode, and an electrolyte which is arranged between the cathode and the anode. The cathode and anode generally comprise metallic current collectors and an active material, which can be the current collector material itself. An electrochemical cell that produces electricity as a result of a spontaneous chemical reaction is called a galvanic cell. An electrochemical element or cell in which a non-spontaneous chemical reaction is driven by an external current source is called an electrolytic cell.

An electrolyte is a compound, or combination of compounds, capable of conducting electricity in the form of an ionic current, carried by mobile ions. Examples of an electrolyte are a salt, or a mixture of salts, in its solid or molten state or dissociated into its ions in a solvent in which the solvent is not or only slightly dissociated.

Electrochemical elements may be configured as a primary battery or a rechargeable battery or an electrochemical capacitor. Rechargeable batteries are often referred to as secondary batteries and non-rechargeable batteries are often referred to as primary batteries.

A battery is a device that stores electrical energy using one or more electrochemical cells. The cells can be connected in series or parallel. The physical

construction of a cell is such that a direct reaction of the chemicals stored in the electrodes is prohibited by physically separating the electrodes by an electrolyte. When the two electrodes are connected through an external 5 circuit, a galvanic cell will produce an electrical current. Electrons will flow through the external circuit, ions will flow through the electrolyte.

The reactions at the electrodes, involving transfer of electrons from one substance to another and thus the 10 reduction and oxidation of the substances, are called redox reactions. The electrode where oxidation takes place is called the anode, the electrode where reduction takes place is called the cathode.

A rechargeable battery is a battery or 15 electrochemical cell in which the chemical reaction, producing the electrical current upon discharge, is easily chemically reversible. A rechargeable battery can be recharged by applying an electrical current to its electrodes or terminals. Preferably, a rechargeable 20 battery can be recharged hundreds of times without significant loss of storage capacity. A primary battery can be discharged only once and has to be disposed off afterwards.

The active material of the positive electrode in a 25 primary battery will be reduced in the discharge process and is therefore also known as the cathode material. Vice versa is material at the negative electrode known as the anode material. The same naming convention is used for the active materials of a rechargeable battery in its 30 charged state (a galvanic cell).

Batteries are widely used as a source of electrical energy for a variety of applications. Rechargeable batteries are used for many applications to avoid the

replacement and disposal of primary batteries. Moreover, their use allows the remote operation of devices in difficult to reach locations where exchange of primary batteries is not practically possible but where
5 recharging a battery would be feasible. An example of such a location is in a wellbore for oil and gas production. Not only are downhole locations difficult to reach, the environmental conditions are also harsh with temperatures in the range of 60 to 200 °C which demands
10 an electrochemical element suitable for high temperatures.

Most batteries are configured for use in a specified temperature range, which is typically capped due to instability, disintegration, melting and/or evaporation
15 of the chemical compounds in the battery above a certain temperature. A typical operating range for batteries is between -40 and +60 °C.

Many rechargeable battery chemistries have been developed. Examples are Lead-acid, Nickel-Cadmium,
20 Nickel-metalhydride, and Lithium (Lithium-metal and Lithium-ion) batteries. From these, batteries based on Lithium chemistry are most interesting since they offer the highest energy density because Lithium has the lowest reduction potential known (-3.045 V versus a standard hydrogen electrode) and has a high specific storage capacity of 3828 mAh/g (for a Lithium 7 isotope=⁷Li).
25 However, the formation of Lithium dendrites on the Lithium anode in rechargeable batteries with electrolytes based on organic solvents has been a safety concern. This
30 has led to the development of Lithium-ion batteries (Li-ion) in which the Lithium anode has been replaced with an intercalation material.

An intercalation or insertion compound is a host compound in which a guest species can be stored or from which it can be extracted. Examples of three dimensional intercalation materials are LiMn_2O_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which reversibly allow the extraction and/or insertion of Lithium ions as guest species from/in their cubic crystal lattice structures.

An intercalation-reaction or insertion-reaction is defined as a reaction, generally reversible, that involves the introduction or removal of a guest species into or from a host structure without a major structural modification of the host. In the strictest sense, intercalation refers to the insertion of a guest into a two-dimensional host; however, the term also now commonly refers to one-dimensional and three-dimensional host structures. An example is the insertion of Lithium into layered TiS_2 : $x \text{ Li} + \text{TiS}_2 \rightarrow \text{Li}_x\text{TiS}_2$ ($0 \leq x \leq 1$) (this example is described in the IUPAC Compendium of Chemical Terminology, 2nd Edition, 1997). Here, x is the variable amount of Lithium intercalated in TiS_2 . The given limits ($0 \leq x \leq 1$) indicate the compositional range over which x can be varied in a reversible way. Between these limits, Li_xTiS_2 exhibits a specific potential curve as function of x when measured versus a suitable reference electrode, which is Lithium metal in case of Lithium intercalation. Many reversible intercalation materials are known, each having a specific potential curve associated with a specific reversible composition range ($x_{\min} \leq x \leq x_{\max}$). These potential curves can be characterised by a lower- and an upper reversible-potential-limit (RPL_{low} and RPL_{upp} , respectively) and an average potential V_{avg} . Some examples are given in table 1.

Table 1. Intercalation materials with reversible composition range and associated capacity, RPL_{low}, average-potential, and RPL_{upp} versus Li/Li⁺. Potentials for Mg_xMo₃S₄ are versus Mg/Mg²⁺.

Material	(x _{min} ≤ x ≤ x _{max})	C (Ah/kg)	RPL _{low} (V)	V _{avg} (V)	RPL _{upp} (V)
Li _{1+x} CrTiO ₄	0 ≤ x ≤ 1	157	1.0	1.5	2.0
Li _{4+x} Ti ₅ O ₁₂	0 ≤ x ≤ 3	175	1.05	1.55	2.05
Li _{4+x} Mn ₅ O ₁₂	0 ≤ x ≤ 3	161	2.4	2.9	3.3
Li _x TiS ₂	0 ≤ x ≤ 1	240	1.5	2.1	2.5
Li _{1+x} Ni _{0.5} Mn _{1.5} O ₄	0 ≤ x ≤ 1	146	2.5	2.9	3.3
Li _{1+x} Mn ₂ O ₄	0 ≤ x ≤ 1	148	2.5	2.9	3.3
Li _{1-x} FePO ₄	0 ≤ x ≤ 1	160	3.0	3.4	3.8
Li _{1-x} Mn ₂ O ₄	0 ≤ x ≤ 0.8	120	3.5	4.1	4.2
Mg _x Mo ₃ S ₄	0 ≤ x ≤ 1	120	0.2	1.1	2.0

The potentials measured versus Mg/Mg²⁺ can easily be converted to potentials versus Li/Li⁺ by using the known reduction potentials versus the standard hydrogen electrode (SHE): Li⁺ + e = Li -3.045 V and Mg²⁺ + 2e = Mg -2.375 V. This means that the upper cut-off potential of Mg_xMo₃S₄ of 2.0 V versus Mg/Mg²⁺ becomes 2.67 V versus Li/Li⁺.

In the field of batteries, it is common to use so called lower- and upper cut-off potentials. These do not necessarily coincide with the RPL potentials of the active materials used. The cut-off potentials are a means of controlling the composition of the intercalation material in a battery and determine the utilisation of

the storage capacity. Setting the cut-off potentials to a window wider than the window defined by the RPL values may result in the irreversible oxidation or reduction of the active materials and/or the electrolyte, leading
5 ultimately to failure of the battery. Setting the cut-off potentials to a window smaller than the RPL window results in a lower utilisation of the storage capacity of the active materials, but in general leads to a longer battery life. The current state-of-the-art Lithium and
10 Li-ion batteries comprise positive electrode (cathode) materials like MnO_2 , $LiCoO_2$, $LiNi_{0.8}Co_{0.2}O_2$, and $LiMn_2O_4$. Carbonaceous materials like graphite, MCMB, and petroleum coke are used as negative (anode) materials in Li-ion batteries. Batteries made by a combination of such
15 cathode and anode materials show attractive high voltages between 3 and 4 V.

The electrolytes used in these batteries are based on Lithium salts as for example $LiPF_6$, $LiBF_4$, $LiClO_4$, and
20 $LiAsF_6$ dissolved in (mixtures of) organic solvents like for example ethylene-carbonate (EC), di-methyl-carbonate (DMC), propylene-carbonate (PC), ethyl-methyl-carbonate (EMC) etc. These solvents are flammable and show considerable vapour pressures at temperatures above 60 °C. Furthermore, these electrolytes can strongly react
25 with the other battery components if the battery temperature rises above 60 °C, for example in the case of over-charging or internal shorting, imposing a potential danger. The operating temperature range is therefore limited from about -40 °C to +80 °C, which is similar to
30 that found for the aqueous electrolytes.

Rechargeable battery chemistries that are able to operate at higher temperatures can be found in the molten

salt systems, for example the system Li//FeS₂ which, depending on the composition of the electrolyte, operates between 350 and 550 °C, or the system Na//S which operates between 220 and 350 °C. Therefore, there is a
5 gap in the operating temperature range of current rechargeable battery technology between about 80 and 220 °C. The reason for this gap lies in the inadequate thermal properties of the available electrolytes.

The current technology of primary batteries, however,
10 does not show such a temperature gap. The system Li//SO₂Cl operates between -40 and +150 °C or, by alloying Lithium with Magnesium, between 70 to 200 °C. In this battery chemistry the electrolyte is the in-situ reaction product when Lithium metal contacts SO₂Cl.
15

International patent application WO 01/15258 (D.R. MacFarlane et al.) discloses a solid-state conductive material comprising a pyrrolidinium or other cation. It further discloses that an anode of a Lithium battery may comprise a Lithium intercalation material.
20

Recent advances in the research of so called ionic liquids have shown that these materials have very promising properties to be used for a new generation of battery electrolytes, especially for high temperature batteries. Ionic liquids are known and have gained a lot
25 of attention for their suitability in green chemistry. In contrast to the organic solvents, ionic liquids are non-flammable, non-volatile, and are chemically stable over a wide temperature range, up to 400 °C. Furthermore, they can be mixed with a wide range of electrolyte salts, allowing very high electrolyte salt concentrations. The conductivities of these electrolytes is comparable or sometimes higher than comparable organic solvent based
30

systems. Many of the ionic liquids are in their liquid state in a wide temperature range, starting below room temperature and ranging up to about 400 °C.

An article by D.R. MacFarlane, et al., (Journal of Phys. Chem. B, 103 (20) 1999, 4164) discloses that, among the known ionic liquids, some members of the pyrrolidinium family of ionic liquids show the widest electrochemical stability windows of up to 5.5 V, measured between glassy-carbon electrodes at 25 °C. The electrolyte stability window is the potential range, bounded by an oxidation- and a reduction-potential, in which the electrolyte is not oxidised nor reduced.

It is known for organic-solvent based electrolytes that a wider stability window is found when inert electrodes are used, like glassy-carbon or Platinum, than when electrodes containing active materials are used, like intercalation compounds. In that case, smaller electrolyte stability windows are found due to interaction of the electrolyte with the active materials. Furthermore, increasing the temperature enhances these interactions, resulting in an even smaller stability window. The large stability window of the pyrrolidinium based ionic liquids renders them as especially interesting for the application in electrolytes for use at high temperatures.

It is known that ionic liquids may be used as an electrolyte in electrochemical elements if an electrolyte salt (e.g. a Lithium salt) is added to the ionic liquid in order to obtain ionic conductivity of the required ion. The term ionic liquid is not well defined in literature but refers in general to a molten salt or to a liquid which consists of fully or almost fully dissociated ions. Room temperature ionic liquids are thus

ionic liquids that are in the liquid state at room temperature. 'Room temperature' is often defined as a temperature close to 25 °C but can be as high as 80 °C. It has to be noted therefore that not all compounds 5 classified as 'ionic liquids' in the open literature have a melting point below 80 °C.

In this specification and claims 10 ionic liquids are defined as 'ionic compounds', which are liquid in the operating temperature range. An ionic liquid may comprise a liquid mixture of ionic compounds.

It is known that in electrochemical elements that are configured for use at temperatures below 60 °C the electrolyte layer may comprise an extensive range of materials with 15 ionic conductivity, such as electrolyte solutions comprising salts, which are dissociated into ions when dissolved in a solvent.

US patent 5,827,602 (Covalent Associates, Inc.) discloses the hydrophobic ionic liquids based on cations comprising pyridinium, pyridazinium, pyrimidinium, 20 pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, and triazolium. Also disclosed is the use of these ionic liquids in an electrochemical cell or a capacitor. No evidence of a stable functioning rechargeable battery incorporating these ionic liquids is shown and no operating temperature range is claimed. 25

US patent 5,965,054 (Covalent Associates, Inc.) discloses the use of the hydrophobic ionic liquids based on cations comprising pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, 30 thiazolium, oxazolium, and triazolium in an electrolyte with a salt dissolved in a polar organic liquid or dissolved in liquid sulfur dioxide. The use of a polar solvent renders the known electrolyte not suitable for

high temperature applications due to vapour formation. No evidence of a stable functioning rechargeable battery incorporating these ionic liquids is shown and no operating temperature range is claimed.

5 US patent 6,326,104 (Electrochemical Systems, Inc.) discloses the use of electrolytes based on ionic liquids comprising the pyrazolium cation. This prior art reference provides four examples related to Lithium rechargeable batteries (a LiMn₂O₄ cathode and a Lithium metal anode), wherein one cell was tested at 55 °C and three cells were tested at room temperature. All cells showed lower than expected capacities and/or fading, i.e. only an indication is given of the potential use. Also, a description was given that the following ionic liquids
10 were not stable against metallic Lithium: 1-ethyl-3-methyl-imidazolium-tetrafluoroborate and 1,2-dimethyl-3-propylimidazolium-tetrafluoroborate.
15

US patent 5,855,809 (Arizona Board of Regents) discloses the use of electrolytes based on the following 20 ionic liquids: X₃PNPOX₂, X₃PNCH₃, X₃PNSO₂X, XS0₂CH₃, CH₃COX, and CH₃CH₂NPX₃ where X is a halogen atom. The results of one battery test are shown for a cell comprising a LiMn₂O₄ cathode and a Lithium metal anode with 0.3LiAlCl₄ in 0.7(AlCl₄⁻/SO₂NPCl₃⁺) as the 25 electrolyte. However, FIG 16 in this patent is not showing the known voltage profile as function of x for a cell with a Li_xMn₂O₄ (0≤x≤1) cathode and a Lithium metal anode. Moreover, the charge capacity is twice the discharge capacity which means that the efficiency is
30 poor. It was further indicated that this cell behaviour was reversible over 50 cycles.

US patent 6,552,843 (Innovative Technology Licensing LLC) discloses a reversible electrodeposition device for controlling the propagation of electromagnetic radiation comprising an electrolyte based on ionic liquids
5 comprising a cation based on N-methyl-pyrrolidinium, pyrrolidinium, 1-ethyl-3-methyl-imidazolium, 1-N-butyl-pyridinium, 2-methyl-1-pyrrolinium or 1-ethyl-imidazolium. A reversible electrodeposition device is an electrochemical device that can only operate as an
10 electrolytic cell. Furthermore, the electrodes do not contain intercalation materials.

International patent application WO 02/063073 (B.R. Mattes, W. Lu) discloses the use of ionic liquids in electrochemical devices with conjugated polymers as
15 the active materials in the electrodes. The cation of the ionic liquid is based on pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, ammonium, pyrrolidinium, pyrrolinium, pyrrolium, and piperidinium.
20 Conjugated polymers are polymer materials with alternating single and double bonds along the polymer chain. No battery related data are disclosed in this prior art reference.

Electrochemical elements for use at a temperature above +60 °C are known from International patent applications WO 0180344 and WO 0209215. The known electrochemical elements comprise a granular electrolyte layer, which is substantially free of polymer binder materials that would evaporate at an elevated
25 temperature. A disadvantage of the use of a granular electrolyte layer is that the physical contact surfaces between the granules are relatively small, which results in a limited transfer of ions via the granules between
30

the cathode and anode, and in a moderate electric power output of the element. The batteries known from these prior art references are suitable for use at a temperature up to about 100 °C and have a limited output 5 of electric power, which is expected to be a result of the limited contact areas between the solid state particles in the electrolyte.

International patent application WO2004/082059 discloses various pyrrolidinium based room temperature 10 ionic liquids for use in energy storage devices, such as secondary lithium batteries.

The referenced prior art shows that ionic liquids can be used to make electrolytes.

Applicant now has discovered that only certain 15 combinations of active materials and electrolytes comprising a pyrrolidinium based ionic liquid result in reversibly operating rechargeable batteries, especially at temperatures between 60 and 150 °C.

It is an object to provide an electrochemical element 20 which is suitable for use at a high temperature.

It is a further object of the present invention to provide an electrochemical element which is suitable for use as a rechargeable battery, which can be used as an efficient energy source at a temperature above 50 °C, in 25 particular in the range from 60 to 150 °C.

It is a further object of the present invention to provide a method for generating electrical energy by means of a rechargeable battery in an underground wellbore, such as an oil or gas production well, in which 30 the temperature may be between 60 and 200 °C or a geothermal well in which the temperature may be up to several hundred degrees Celsius.

SUMMARY OF THE INVENTION

The electrochemical element according to the invention comprises a cathode, an anode and an electrolyte arranged between the cathode and anode, which electrolyte comprises an ionic liquid comprising an anion and a cation, which cation comprises a pyrrolidinium ring structure; and wherein the active material of the cathode comprises an intercalation material having an upper reversible-potential-limit of at most 4 V versus Li/Li⁺.

Applicant has discovered that intercalation materials with an upper reversible-potential-limit of more than 4 V versus Li/Li⁺ are not suitable for reversible use. It is believed that the interaction between the electrolyte and these materials cause degradation of the materials and/or electrolyte resulting in loss of capacity, especially when used at temperatures above 70 °C.

Suitable intercalation materials with an upper reversible-potential-limit of at most 4 V are for example: LiFePO₄, Li₃Fe₂(PO₄)₃, Li₄Mn₅O₁₂, Li₂Mn₄O₉, MnO₂, FeS₂, LiV₃O₈, V₂O₅, TiS₂, TiO₂, Li₂Ti₃O₇, LiTi₂(PO₄)₃, NaTi₂(PO₄)₃, TiP₂O₇, LiV₂O₄, Li₄Ti₅O₁₂, LiCrTiO₄, LiTi₂O₄, CuO, MgMo₃O₄, Li₃FeN₂, Li₇MnN₄. Particularly suitable intercalation materials are LiFePO₄, Li₄Mn₅O₁₂, TiS₂, Li₄Ti₅O₁₂ and LiCrTiO₄.

It is observed that WO 01/15258 discloses a solid-state conductive material comprising a pyrrolidinium or other cation. It further discloses that an anode of a Lithium battery may comprise a Lithium intercalation material.

It is believed that a solid-state conductive material has a lower ionic conductivity than an ionic liquid. The use of an ionic liquid in the electrochemical element

according to the present invention instead of a solid-state conductive material will result in a higher power density and therefore in a better performance of the electrochemical element.

5 When used in this specification and claims an active intercalation material is defined as an intercalation material that takes part in the redox reaction in the electrodes.

10 As an alternative to the use of an active intercalation material the anode of an electrochemical element may comprise a conjugated polymer. International patent application WO/02/063073 discloses an electrochemical element with an anode or cathode comprising a conjugated polymer as the major constituent 15 of the active material.

20 The electrochemical element according to the invention may be configured for use as a primary or a rechargeable battery or an electrochemical capacitor at high temperature, such as a temperature above 50 °C and particularly at a temperature between 60 and 150 °C. It is furthermore preferred that the pyrrolidinium ring structure has the formula: N-R₁-N-R₂-pyrrolidinium, wherein R₁ and R₂ are alkyl groups and that R₁ is methyl and R₂ is butyl or hexyl.

25 The anion of the ionic liquid preferably comprises any of the following compounds:

- ClO₄⁻, AsF₆⁻, PF₆⁻, BF₄⁻, a halogen ion, N(CF₃)₂⁻, N(CF₃SO₂)₂⁻ ('TFSI'), CF₃SO₃⁻, and N(CH₃SO₂)₂⁻, N(C₂F₅SO₂)₂⁻, B(C₂O₄)₂⁻, C(CF₃SO₂)₃⁻.

It is also preferred that the alkali salt comprises a Lithium salt which may comprise any of the following compounds:

- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ('LitFSI'), LiCF_3SO_3 , LiClO_4 , LiBF_4 ,
- 5 LiPF_6 , and LiAsF_6 , $\text{LiB}(\text{C}_2\text{O}_4)_2$, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$.

Alternatively the salt may comprise MgCF_3SO_2 or $\text{Mg}(\text{ClO}_4)_2$.

The cathode suitably comprises $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{4-y}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ ($0 \leq y \leq 1$), LiCrTiO_4 , V_2O_5 , TiS_2 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$, $\text{Li}_{4-y}\text{Mg}_y\text{Mn}_5\text{O}_{12}$ ($0 \leq y \leq 1$) or $\text{Li}_{1-y}\text{M}_y\text{FePO}_4$, where M=Mg, Nb, Zr, Ti or Al ($0 \leq y \leq 0.02$), as the active material and as the major constituent by mass.

The anode suitably comprises Lithium, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{4-y}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ ($0 \leq y \leq 1$), LiCrTiO_4 , as the active material.

15 The invention also provides a method of providing electrical energy in an underground wellbore, wherein the energy is provided by an electrochemical element according to the invention. The underground wellbore may form part of an oil and/or gas production well or a geothermal well.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described in more detail with reference to the accompanying drawings wherein:

FIG. 1 A,B and C depict three examples of 25 pyrrolidinium cations comprising a ring structure of four Carbon atoms and one Nitrogen atom;

FIG. 2 is a graph showing charge and discharge capacity of the cell with a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cathode and a Lithium metal anode 110 °C with LitFSI in P_{14}TFSI in the 30 molar ration 0.38:0.62. The capacity is given as

percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 3 is a graph showing voltage curves for cycle number 7, 107 and 207 of the cell with a Li₄Ti₅O₁₂ cathode and a Lithium metal anode 110 °C with LiTFSI in P₁₄TFSI in the molar ration 0.38:0.62;

FIG. 4 is a graph showing charge and discharge capacity of the cell with a Li₄Ti₅O₁₂ cathode and a Lithium metal anode 110 °C with 2.0 mol/kg LiTFSI in P₁₆TFSI. The capacity is given as percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 5 is a graph showing charge and discharge capacity of the cell with a TiS₂ cathode and a Lithium metal anode 110 °C with LiTFSI in P₁₄TFSI in the molar ration 0.40:0.60. The capacity is given as percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 6 is a graph showing voltage curve for cycle 50 of the cell with a TiS₂ cathode and a Lithium metal anode 110 °C with LiTFSI in P₁₄TFSI in the molar ration 0.40:0.60;

FIG. 7 is a graph showing charge and discharge capacity of the cell with a Li₄Ti₅O₁₂ cathode and a Lithium metal anode 150 °C with LiTFSI in P₄₄TFSI in the molar ration 0.30:0.70. The capacity is given as percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 8 is a graph showing the potential curves of three cells with a LiMn₂O₄ cathode and a Lithium metal anode. Cell A contains a reference electrolyte based on

organic solvents at 25 °C and shows the expected characteristic potential curve. Cells B and C contain pyrrolidinium based electrolytes at 110 °C and show failure of the cells starting; and

5 FIG. 9 shows the characteristic flat potential curve for LiFePO₄ cathode and a Lithium metal anode 110 °C with LiTFSI in P₁₄TFSI in the molar ration 0.40:0.60. The potential is given as function of time.

DETAILED DESCRIPTION OF THE INVENTION

10 FIG. 1A depicts that a pyrrolidinium compound comprises a positively charged ring structure of four carbon atoms and one nitrogen atom. The depicted compound has the formula: N-R₁-N-R₂-pyrrolidinium, wherein R₁ and R₂ are alkyl groups and wherein R₃-R₁₀ are either: H; F; 15 separate alkyl groups which may be branched, substituted and comprise heteroatoms; separate phenyl groups which may be substituted and comprise heteroatoms. In the electrochemical element according to the invention is it preferred that R₁ is methyl and R₂ is butyl or hexyl or 20 that R₁=R₂ is butyl.

FIG. 1B depicts the chemical structure of 1-butyl-1-methyl-pyrrolidinium and FIG. 1C depicts the chemical structure of 1-butyl-2,2,3,3,4,4,5,5-octafluoro-1-methyl-pyrrolidinium.

25 Several rechargeable batteries with electrolytes comprising pyrrolidinium based ionic liquids were made and tested using the manufacturing and testing procedures that are described hereinbelow. Electrolytes were synthesised by mixing pyrrolidinium based ionic liquids and lithium salts. The following acronyms will be used:

P₁₄=1-methyl-1-butyl-pyrrolidinium

P₁₆=1-methyl-1-hexyl-pyrrolidinium

P₄₄=di-butyl-pyrrolidinium

TFSI=bis(trifluoromethylsulfonyl)imide=N(CF₃SO₂)₂⁻

P₁₄TFSI and P₁₆TFSI (acquired from Merck KGaA) were dried under dynamic vacuum at 90 °C for 48 hours. The
5 salts LiTFSI (LiN(CF₃SO₂)₂, 3M) and Lithium-perchlorate (LiClO₄, from Alfa Aesar) were dried under dynamic vacuum at 130 °C for 48 hour. After being dried, the materials were transferred into a helium filled glovebox (water content <5 ppm). The following electrolytes were made by
10 mixing the appropriate amounts of ionic liquid and salt, resulting in clear and stable liquids:

5 mol% LiTFSI in P₁₄TFSI

0.38 mol LiTFSI in 0.62 mol P₁₄TFSI

0.40 mol LiTFSI in 0.60 mol P₁₄TFSI

15 2.0 mol/kg LiTFSI in P₁₆TFSI

1.0 mol/kg LiClO₄ in P₁₄TFSI

0.30 mol LiTFSI in 0.70 mol P₄₄TFSI

Electrodes were made of LiCrTiO₄, Li₄Ti₅O₁₂, LiFePO₄ and TiS₂ and were coated as follows.

20 The electrodes were made by the doctor-blade technique on Aluminium or Copper foil current collectors using a paste of the active materials. The pastes contained typically 80 w% active material, 10-13 w% conductive additives, and 7-10 w% of a binder dissolved
25 in 1-methyl-2-pyrrolidon (Merck KGaA). The conductive additives were a mixture of carbon black (2-10%, SuperP from MMM) and graphite (0-10 w%, KS4 from Timcal). The binder was either polyvinylidenefluoride (PVDF, from Solvay) or polymethylmethacrylate (PMMA). LiCrTiO₄ and
30 LiFePO₄ were synthesised in house, Li₄Ti₅O₁₂ was obtained

from Hohsen Corporation Japan, TiS₂ was obtained from Alfa Aesar, LiMn₂O₄ was obtained from Sedema. The coatings were dried at 140 °C for about 15 minutes, densified using a Durston rolling mill, and further dried 5 overnight under dynamic vacuum at 80 °C. Finally, samples of 15 mm diameter, with a typical capacity of 1-2 mAh, were punched out and used for testing.

All measurement were done using CR2320 type coin cells (23 mm diameter, 2 mm high, 304 steel, acquired from 10 Hohsen Corporation Japan), with polypropylene (PP) or polytetrafluoroethylene (PTFE) gaskets, or in 304 steel cells with high temperature viton O-rings. All cells were assembled in a glovebox. Typically, a cell was made by stacking in a can: an electrode, a 21 mm diameter 15 glassfiber mat (type GF/C, Whatman), a gasket, 4-5 drops of electrolyte with a 1 ml polyethylene pipet, a 17 mm diameter Lithium disk 0.38 mm thick (Chemetall), a 17 mm diameter pressing plate 0.2 mm thick, a 15 mm diameter wave-spring, and a cap which was insulated by tape. If 20 necessary, the electrolyte was warmed to about 100 °C to reduce the viscosity. The cells were closed in a manual CR2320 crimping tool (Hohsen Corporation Japan).

Testing of batteries

The cells were cycled (subsequent charging and 25 discharging) in air in climate chambers (± 0.1 °C accuracy) using Maccor S4000 battery testers. The cells were subjected to various current densities, ranging from 0.1 to 1.0 C-rate. Within a cycle the current was constant and equal for discharging and charging. The 30 1 C-rate is here defined as the current needed to fully discharge the battery in 1 hour as calculated from the mass of active material and its specific storage

capacity. Thus, ideally a 0.1C-rate discharge lasts for 10 hours and a 2.0 C-rate lasts 0.5 hour.

EXAMPLE I:

5 "Testing at 110° of a rechargeable battery with a Li₄Ti₅O₁₂ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in P₁₄TFSI"

10 A coin cell was made according to the procedures described above. Li₄Ti₅O₁₂ was used as the cathode material with PvdF as binder on an Aluminium current collector. The electrolyte was a mixture of LiTFSI dissolved in P₁₄TFSI in the molar ratio of 0.38:0.62. The cell was cycled 242 times between 1.0 and 2.0 V at 110 °C.

15 In the first 29 cycles the current was varied between 0.1 and 1.0 °C. FIG. 2 shows the capacity for discharging and charging as percentage of the expected sample capacity. Very stable cycling behaviour of the battery was found with good rate capability and high efficiency. The voltage curves in FIG. 3 show the typical voltage 20 curve of Li₄Ti₅O₁₂ versus lithium for the 7-th, 107-th and 207-th cycle for the same current density indicating that the active material did not change and did not lose its integrity.

EXAMPLE II:

25 "Testing at 110 °C of a rechargeable battery with a Li₄Ti₅O₁₂ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in P₁₆TFSI"

30 A coin cell was made according to the procedures described above. Li₄Ti₅O₁₂ was used as the cathode material with PvdF as binder on an Aluminium current collector. The electrolyte was a 2.0 mol/kg mixture of

LiTFSI dissolved in P₁₆TFSI. The cell was cycled 150 times between 1.0 and 2.0 V at 110 °C.

In the first 29 cycles the current was varied between 0.1 and 1.0 °C. FIG. 4 shows the capacity for discharging and charging as percentage of the expected sample capacity. Very stable cycling behaviour of the battery was found with good rate capability and high efficiency.

EXAMPLE III:

"Testing at 110 °C of a rechargeable battery with a TiS₂ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in P₁₄TFSI"

A coin cell was made according to the procedures described above. TiS₂ was used as the cathode material with PvdF as binder on an Aluminium current collector. The electrolyte was a mixture of LiTFSI dissolved in P₁₄TFSI in the molar ratio of 0.40:0.60. The cell was cycled 13 times between 1.8 and 2.5 V and 87 times between 1.5 and 2.5 V at 110 °C.

FIG. 5 shows the capacity for discharging and charging as percentage of the expected sample capacity. The lowering of the lower cut-off voltage increased the capacity substantially. Apart from some initial fading the cycling is fairly stable and with high efficiency. The voltage curves in FIG. 6 shows the typical voltage curve of TiS₂ versus lithium for the 50-th cycle.

EXAMPLE IV:

"Testing at 150 °C of a rechargeable battery with a Li₄Ti₅O₁₂ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in P₄₄TFSI"

A coin cell was made according to the procedures described above. Li₄Ti₅O₁₂ was used as the cathode material with PvdF as binder on an Aluminium current

5 collector. The electrolyte was a mixture of LiTFSI dissolved in P₄₄TFSI (di-butyl-pyrrolidinium-TFSI) in the molar ratio 0.30:0.70. The cell was cycled 60 times between 1.0 and 2.0 V at 150 °C. The current was varied between a 0.1, 0.5, and 1.0C-rate.

10 FIG. 7 shows the capacity for discharging and charging as percentage of the expected sample capacity. Even at 150 °C the cycling stability is very good and similar to that at 110 °C demonstrating the use of these electrolytes in high temperature batteries.

EXAMPLE V:

"Testing at 110 °C of a rechargeable battery with a 4.1 V LiMn₂O₄ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in P₁₄TFSI or P₁₆TFSI"

15 Three coincells were made according to the procedures described above. LiMn₂O₄ was used as the cathode material with PvdF as binder on a 304-steel current collector. The electrolytes were:

- 20 A. 1 M LiPF₆ in EC/DMC 2:1 w/w;
B. 0.05 mol LiTFSI dissolved in 0.95 mol P₁₄TFSI
C. 1 mol/kg LiTFSI dissolved in P₁₆TFSI

The cells were charged and discharged between 3.5 and 4.3 V at 25 °C for electrolyte A and at 110 °C for electrolyte B and C. The current was a 0.1C-rate.

25 FIG. 8 shows the potential curves for the three cells. The reference cell with electrolyte A shows the expected characteristic potential curve for LiMn₂O₄ being symmetrical in charge and discharge. The cell with electrolyte B did not reach a potential higher than 4 v and failed. The cell with electrolyte C showed a too small charge capacity and an even smaller discharge

capacity. The specific LiMn_2O_4 potential curve is lost and the capacity faded quickly. These tests demonstrate that the pyrrolidinium based electrolytes cannot be used with intercalation materials which have an upper reversible-potential-limit higher than 4 V versus Li/Li^+ .

EXAMPLE VI:

"Testing at 110 °C of a rechargeable battery with a 3.4 V LiFePO_4 cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in P_{14}TFSI "

A coin cell was made according to the procedures described above. LiFePO_4 was used as the cathode material with PvdF as binder on an Aluminium current collector. The electrolyte was a mixture of LiTFSI dissolved in P_{14}TFSI in the molar ratio 0.40:0.60. The cell was cycled between 3.0 and 3.8 V as the upper cut-off potential at 110 °C. The current was a 0.1C-rate.

FIG. 9 shows the characteristic flat potential curve for LiFePO_4 , being symmetrical for charge and discharge. This test demonstrates that the pyrrolidinium based electrolytes can be used with intercalation materials with an upper reversible-potential-limit up to 4 V versus Li/Li^+ .

EXAMPLES I-VI and FIG. 1-9 demonstrate that the tested cells with pyrrolidinium based ionic liquid electrolytes and with a cathode comprising an intercalation material having an upper reversible-potential-limit (RPL_{upp}) of at most 4 V versus Li/Li^+ are suitable for use as rechargeable batteries at a high temperature of up to at least 150 °C.

The examples further indicate that suitable materials for use in the rechargeable batteries are:

- $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, LiCrTiO_4 , and TiS_2 as active intercalation materials.

It is also believed that other known intercalation materials as for example $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ (~ 2.9 V insertion, $0 \leq y \leq 1/3$), $\text{LiMg}_y\text{Ni}_{0.5-y}\text{Mn}_{1.5}\text{O}_4$ (~ 2.9 V insertion, $0 \leq y \leq 0.5$), $\text{Li}_2\text{Mn}_4\text{O}_9$ (~ 2.9 V insertion), Li_7MnN_4 , and Li_3FeN_2 can be used.

- Aluminium and stainless steel SUS304 as a current collector materials.

It is also believed that other materials as for example Nickel, Copper, Gold, Platinum, Carbon, and Graphite can be used as current collectors.

- PvdF and PMMA as binder materials.

It is also believed that other known binder materials as for example PTFE, PCTFE, ECTFE, ETFE, and FEP can be suitable binder materials.

- Carbon black and graphite as conductive additives.

It is also believed that instead or together with Carbon black and Graphite it is possible to use a metal foam or similar porous but electronically conductive structure, glassy carbon, or a metal powder as a conductive matrix in the electrodes. This can be an advantage in case Carbon black and/or graphite cause unwanted side reactions with other materials in the battery.

- porous glassfiber mat as separator material.

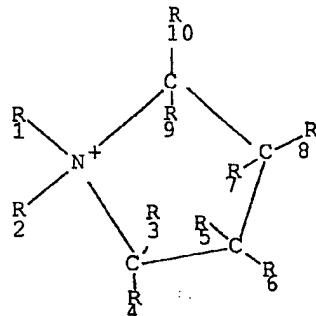
It is also believed that for example porous layers comprising Al_2O_3 , MgO , Li- β -Alumina are suitable separator materials.

Mixtures of P_{14}TFSI , P_{16}TFSI and P_{44}TFSI with LiTFSI and/or LiClO_4 .

C L A I M S

1. An electrochemical element with a cathode, an anode and an electrolyte arranged between the cathode and anode, which electrolyte comprises an ionic liquid comprising an anion and a cation, which cation has a
5 pyrrolidinium ring structure,
and wherein the active material of the cathode comprises an intercalation material having an upper reversible-potential-limit of at most 4 V versus Li/Li⁺.
2. The electrochemical element of claim 1, wherein the
10 electrochemical element is a primary battery or a rechargeable battery or an electrochemical capacitor.
3. The electrochemical element of claim 1 or 2, wherein the electrochemical element is configured for use at a temperature above 50 °C.
- 15 4. The electrochemical element of claim 3, wherein the electrochemical element is configured for use at a temperature between 60 and 200 °C.
5. The electrochemical element of any preceding claim, wherein the pyrrolidinium ring structure has the formula:
20 N-R₁-N-R₂-pyrrolidinium, wherein R₁ and R₂ are alkyl groups.
6. The electrochemical element of claim 5, wherein the pyrrolidinium ring structure has the formula N-methyl-N-butyl-pyrrolidinium.
- 25 7. The electrochemical element of claim 5, wherein the pyrrolidinium ring structure has the formula N-methyl-N-hexyl-pyrrolidinium.

8. The electrochemical element of claim 1, wherein the pyrrolidinium structure is:



wherein R₁-R₁₀ are either: H; F; separate alkyl groups which may be branched, substituted and comprise heteroatoms; separate phenyl groups which may be substituted and comprise heteroatoms.

5

9. The electrochemical element of any preceding claim, wherein the anion of the ionic liquid comprises any of the following compounds:

10 ClO₄⁻, PF₆⁻, BF₄⁻, AsF₆⁻, a halogen ion, N(CF₃)₂⁻, N(CF₃SO₂)₂⁻, CF₃SO₃⁻, N(CH₃SO₂)₂⁻, N(C₂F₅SO₂)₂⁻, B(C₂O₄)₂⁻, C(CF₃SO₂)₃⁻.

11. The electrochemical element of claim 1, wherein the electrolyte further comprises a salt.

15

11. The electrochemical element of claim 10, wherein the salt comprises an alkali salt, particularly a Lithium salt, more particularly a Lithium salt comprising any of the following compounds:

20

- LiN(CF₃SO₂)₂, LiCF₃SO₃, LiClO₄, LiBF₄, LiPF₆, or LiAsF₆.

12. The electrochemical element of claim 10, wherein the salt comprises MgCF₃SO₂ or Mg(ClO₄)₂.

13. The electrochemical element of any preceding claim, wherein the active material of the cathode comprises an intercalation material as the major constituent by mass.

5 14. The electrochemical element of claim 13, wherein the cathode comprises as the major constituent by mass of the active material any of the following compounds:

$\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiTi_2O_4 , $\text{Li}_{4-y}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ ($0 \leq y \leq 1$), V_2O_5 ,

$\text{Li}_4\text{Mn}_5\text{O}_{12}$, $\text{Li}_{4-y}\text{Mg}_y\text{Mn}_5\text{O}_{12}$ ($0 \leq y \leq 1$).

10 15. The electrochemical element of claim 13, wherein the cathode comprises LiCrTiO_4 as the major constituent by mass of the active material.

16. The electrochemical element of claim 13, wherein the cathode comprises TiS_2 as the major constituent by mass of the active material.

15 17. The electrochemical element of claim 13, wherein the cathode comprises $\text{Li}_{1-y}\text{M}_y\text{FePO}_4$, where $\text{M}=\text{Mg, Nb, Zr, Ti, Al}$ and ($0 \leq y \leq 0.02$), as the major constituent by mass of the active material.

20 18. The electrochemical element of claim 1, wherein the anode comprises Lithium metal as the major constituent by mass of the active material.

19. The electrochemical element of claim 1, wherein the anode comprises as the major constituent by mass of the active material any of the following compounds:

25 $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiCrTiO_4 , LiTi_2O_4 , $\text{Li}_{4-y}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ ($0 \leq y \leq 1$).

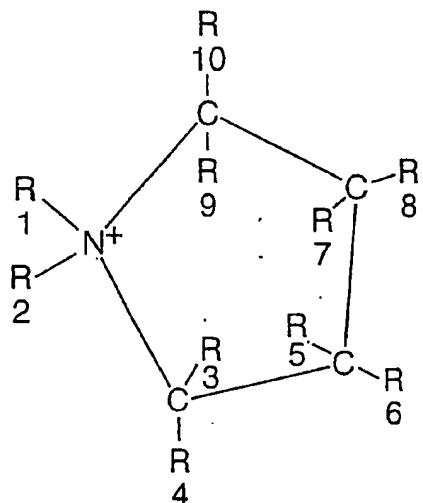
20 20. The electrochemical element of claim 1, wherein the cathode comprises as the major constituent by mass of the active material $\text{Li}_{1-a}\text{FePO}_4$ ($0 \leq a \leq 1$) and wherein the anode comprises as the major constituent by mass of the active material $\text{Li}_{(4-y)+b}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ ($0 \leq b \leq 3$ and ($0 \leq y \leq 1$)).

30 21. The electrochemical element of claim 1, wherein the cathode comprises as the major constituent by mass of the

active material $\text{Li}_{(4-y)+a}\text{Mg}_y\text{Mn}_5\text{O}_{12}$ ($0 \leq a \leq 1$ and $0 \leq y \leq 1$) and wherein the anode comprises as the major constituent by mass of the active material $\text{Li}_{(4-y)+b}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ ($0 \leq b \leq 3$ and $0 \leq y \leq 1$).

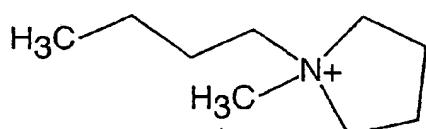
- 5 22. The electrochemical element of claim 1, wherein the cathode and/or anode comprises polyvinylidenefluoride (PVDF) as a binder material.
- 10 23. The electrochemical element of claim 1, wherein the cathode and/or anode comprises polytetrafluoroethylene (PTFE) as a binder material.
- 15 24. A method of providing electrical energy in an underground wellbore, wherein the energy is provided by an electrochemical element according to any preceding claim.
- 20 25. The method of claim 24, wherein the wellbore forms part of an oil and/or gas production well or a geothermal well.
26. The method of claim 24, wherein the wellbore forms part of an oil and/or gas production well and oil and/or gas is produced through the well and wherein the flow of oil and/or gas is monitored and/or controlled by electric downhole monitoring and/or control equipment which is powered by an electrochemical element according to any one of claims 1-23.

Fig.1A. Pyrrolidinium cations



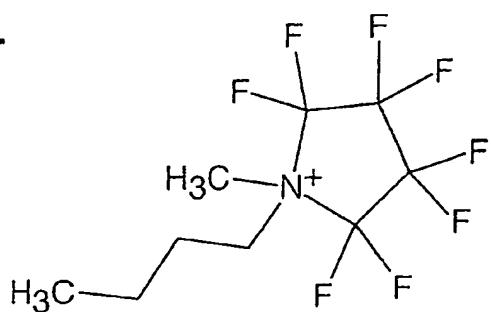
pyrrolidinium ring structure:
R₁-R₁₀ is e.g. H, F, alkylgroup, etc.

Fig.1B.



1-butyl-1-methylpyrrolidinium

Fig.1C.



1-butyl-2,2,3,3,4,4,5,5-octafluoro-1-methylpyrrolidinium

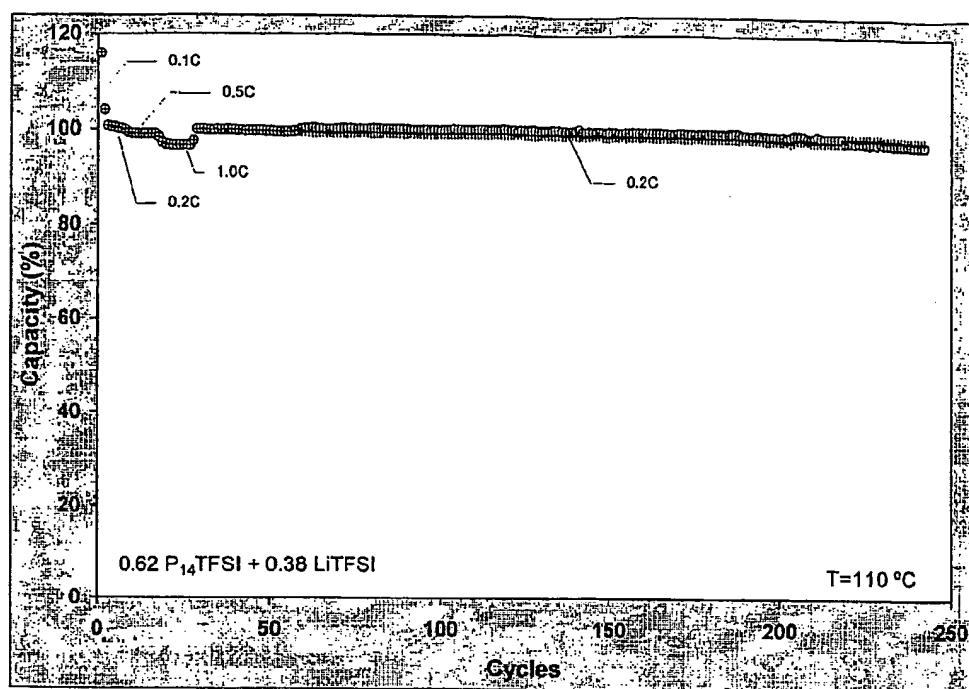


FIG 2

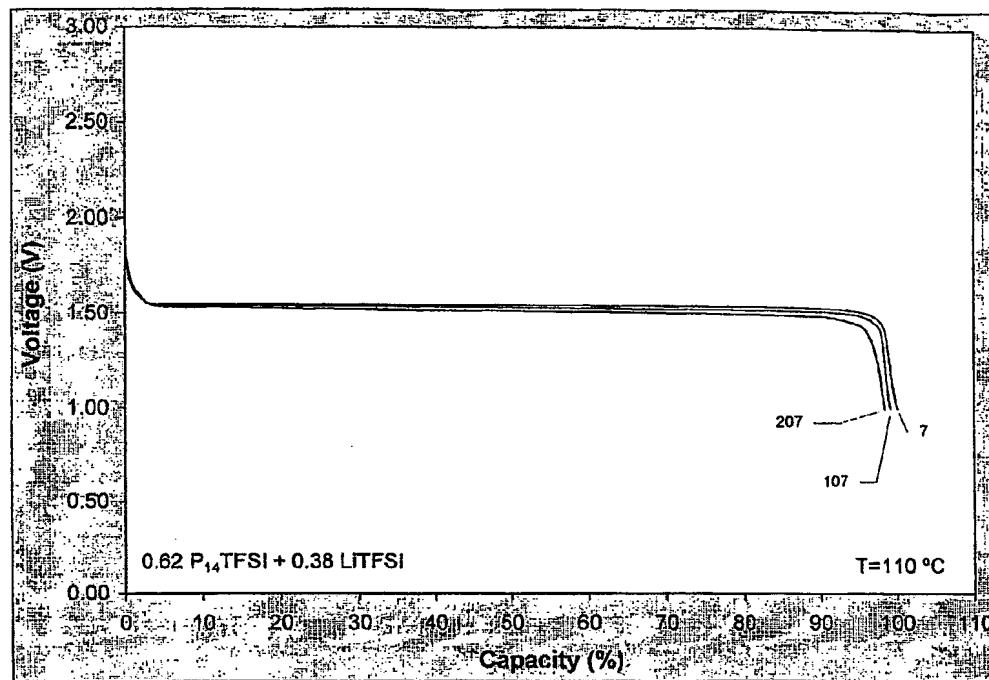


FIG 3

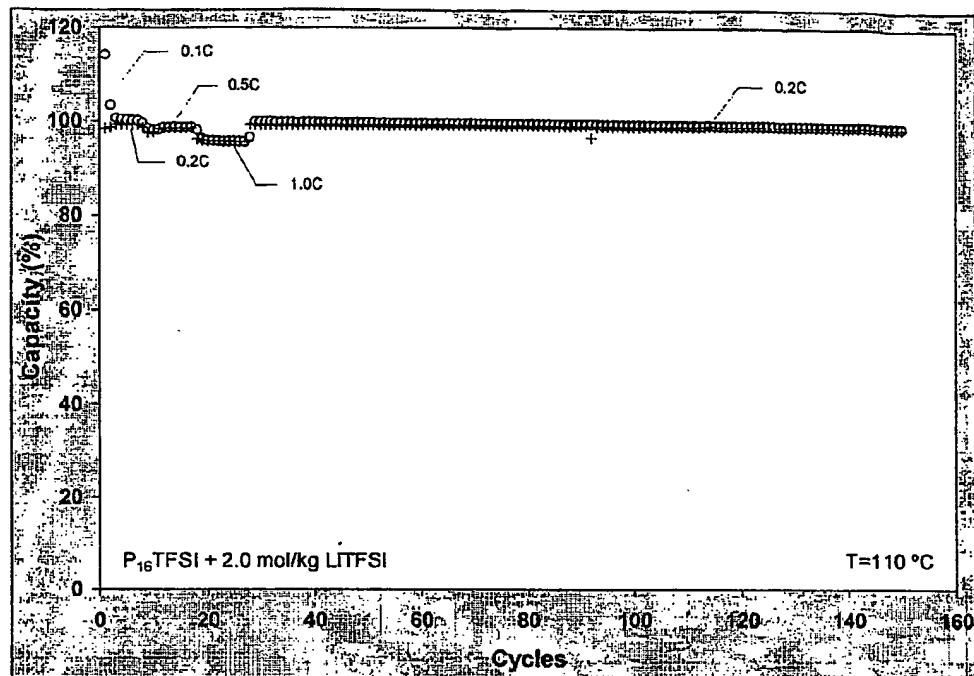


FIG 4

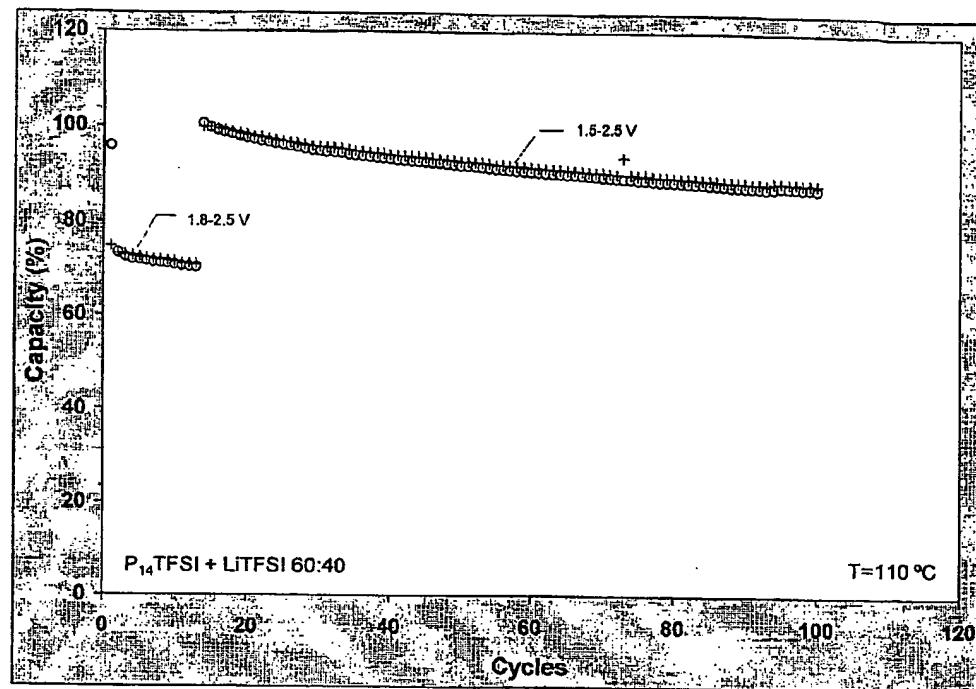


FIG 5

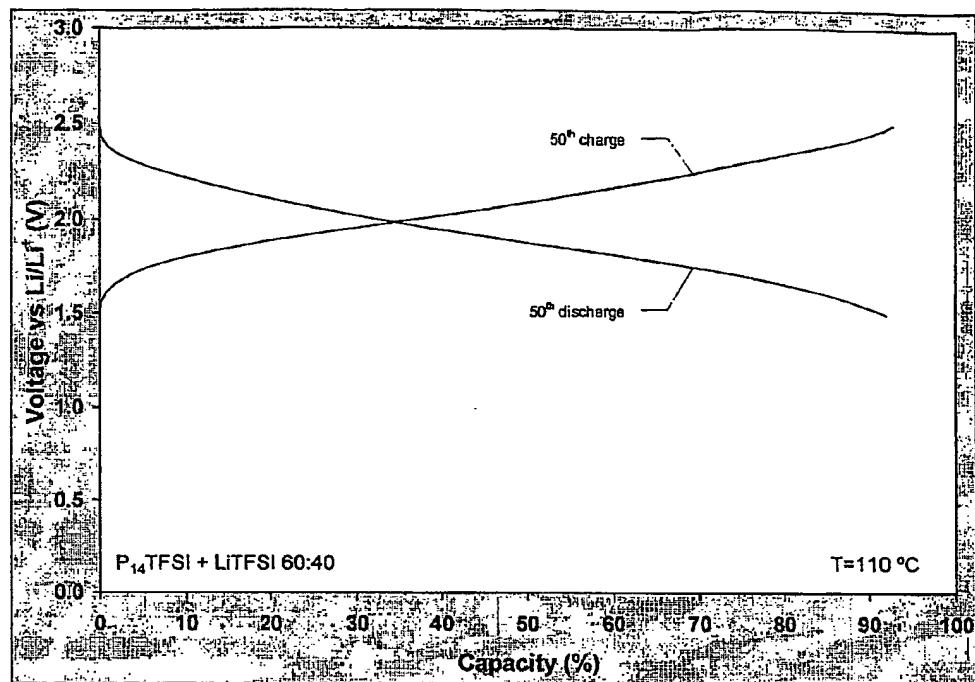


FIG 6

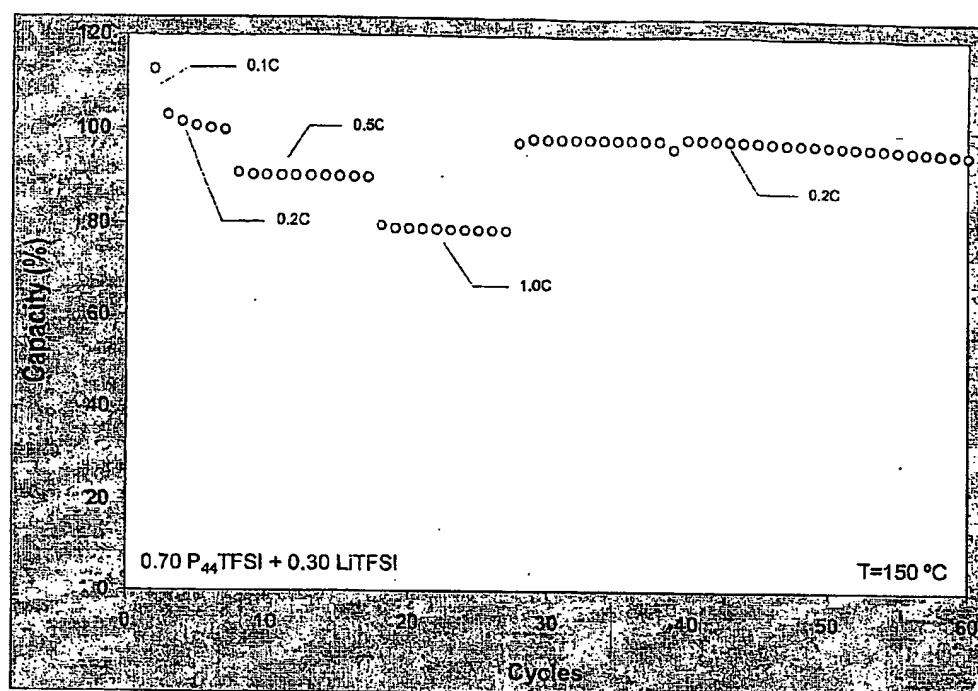


FIG 7

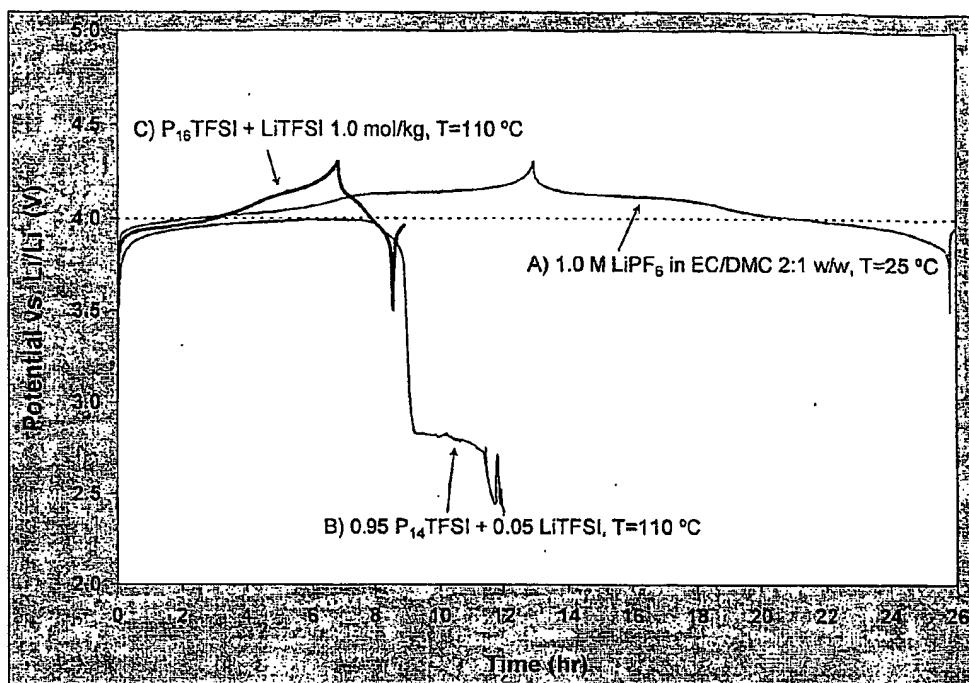


FIG 8

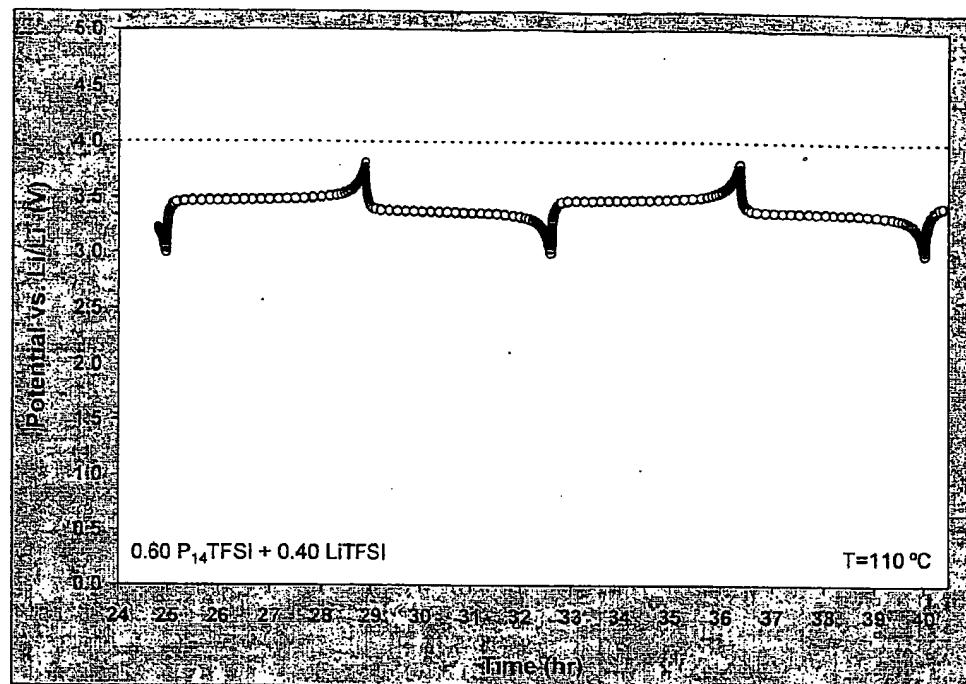


FIG 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/053182

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M10/40 H01M10/39 H01M10/36 H01M6/14 H01M6/16
H01G9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/15258 A (MONASH UNIVERSITY; MACFARLANE, DOUGLAS, ROBERT; FORSYTH, MARIA; HUANG,) 1 March 2001 (2001-03-01) cited in the application	1-26
A	MACFARLANE D R ET AL: "Pyrrolidinium imides: a new family of molten salts and conductive plastic crystal phases" 20 May 1999 (1999-05-20), JOURNAL OF PHYSICAL CHEMISTRY. B, MATERIALS, SURFACES, INTERFACES AND BIOPHYSICAL, WASHINGTON, DC, US, PAGE(S) 4164-4170 , XP002211103 ISSN: 1089-5647 cited in the application	1-26
A	US 2002/055045 A1 (MICHTH CHRISTOPHE ET AL) 9 May 2002 (2002-05-09)	1-26

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Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

18 February 2005

11/03/2005

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Götz, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/053182

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